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by

VICTOR ELLIOTT WELLMAN
Du Pont Fellow, 1928-1929

L. C.

A Thesis Submitted in Partial Fulfilment of the Requirements for the Degree of Doctor of Philosophy

Reprinted from the Journal of Physical Chemistry, Vol. XXXIV, pp. 379-409, 1930

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A STUDY OF FACTORS CONTROLLING TYPE OF WATER-SOAP-OIL EMULSIONS

Introduction

The complexity of emulsions is revealed by the many factors which influence their type and stability. The literature[1] on emulsions stabilized with soaps leads almost to confusion because of the variety of factors reported to influence stability and to determine type. There is almost complete agreement, however, on the following: (1) alkali soaps stabilize only oil-in-water emulsions, (2) polyvalent soaps stabilize only water-in-oil emulsions, (3) emulsification is aided by low interfacial tension between the phases and (4) the charge carried by the droplets influences emulsion stability. The purpose of the present investigation was to examine some of these fundamental concepts; the results indicate that the tendency has been to generalize too freely, and that emulsion characteristics cannot be predicted until the exceedingly difficult problem of interrelating the various influential factors has been solved.

Preparation of Materials

The value of much of the literature dealing with emulsions stabilized by soaps, has been vitiated through the use of materials of questionable purity, and the uncertainty resulting from the use of mixtures such as olive oil, etc. The elimination of these uncertainties will permit a more accurate interpretation of the phenomena observed. Consequently, all materials used in the quantitative part of this work were carefully purified.

Purification of Benzene.

Benzene of "C.P. Analyzed" quality, b. p. 80° was allowed to stand in contact with concentrated sulfuric acid, with occasional shaking, until the absence of thiophene was shown by the test with isatin and sulfuric acid. The benzene was then washed free from acid with distilled water and dried over calcium chloride. When distilled, the fraction passing over between the corrected temperatures 79.96° to 80.06° was taken. The benzene was used only once.

Preparation of Soaps.

Sodium Oleate. Merck's U. S. P. oleic acid, having an iodine number of 89.9 was purified by the method used by Harkins and Zollman.[2] To an

[1] References to literature must necessarily be made in the body of the report in order that they appear relevant; the subject is too broad to be clearly and conveniently treated as a unit.

[2] Harkins and Zollman: J. Am. Chem. Soc., **48**, 69 (1926). It later became known that Lapworth, Pearson and Mottram: Biochem. J., **19**, (1925), have shown that this method does not insure the purity of the oleic acid obtained if palmitic acid is present.

alcoholic (95 percent ethyl alcohol) solution of the oleic acid was slowly added, with stirring, a filtered solution of alcoholic sodium hydroxide until a slight excess of the alkali was present. Complete neutralization was accomplished by refluxing the mixture for thirty minutes, after which the hot solution was filtered and the soap allowed to crystallize. The sodium oleate was washed three times with 95 percent ethyl alcohol, and dried between quantitative fllter papers. It was then taken up in another portion of alcohol, refluxed for thirty minutes, filtered and allowed to crystallize as before. After drying with filter paper, the soap was allowed to stand over night in contact with cold absolute alcohol. The alcohol was removed by decantation after which the soap was washed with three small portions of absolute alcohol. Final drying was accomplished by warm air (40°) under reduced pressure. The soap thus obtained was almost white, having only a slight cream tint.

Sodium Stearate. Eastman Kodak Company's stearic acid, m.p. 68.9°, was dissolved in hot alcohol and a slight excess of a filtered solution of C.P. sodium carbonate was slowly added, with stirring. The solution was refluxed for thirty minutes after which it was filtered hot. The gel which formed on cooling was crushed between filter papers until most of the alcohol and soluble impurities had been removed. The soap was again brought into solution in 95 percent ethyl alcohol and filtered, after which the alcohol was evaporated until the soap set to a gel. It was then crushed in a mortar and brought to dryness on a water bath. After being pulverized, the dried soap was washed three times with absolute alcohol and three times with anhydrous ether. The final drying was done in an oven at 90°.

Sodium Palmitate and Potassium Stearate. These soaps were prepared in a manner similar to that used for sodium stearate. The potassium soap, however, did not show such a pronounced tendency to gel.

Calcium Oleate. To a known weight of oleic acid an excess of calcium acetate solution was slowly added with stirring. The precipitated calcium soap was thoroughly washed with water, alcohol and ether. Then it was powdered and rewashed, as before, to remove all traces of the acetate.[1]

Magnesium Oleate and Palmitate, and Barium Oleate. The above method was not found efficacious for the production of these soaps. They were prepared by metathesis of the acetates with the corresponding sodium soaps. Their final washing was carried out as outlined for calcium oleate.

Bivalent Soaps of Some Lower Fatty Acids. Small quantities of magnesium heptylate, magnesium caprylate, magnesium caproate and calcium valerate were made by treating the acids in a small volume of alcohol, with an excess of the carbonates. After removal of the excess carbonates by filtration, the precipitated bivalent soaps were washed with absolute alcohol and then with anhydrous ether.

[1] It was found that just one drop of dilute acid was sufficient to make the calcium easily wetted by water; otherwise it is so little wetted by water that it is difficult to wash.

Miscellaneous Materials.

Water. All water used in these experiments was distilled water and had an average conductivity of 5×10^{-6} mhos.

Shaker. The mechanical shaker employed was that used by Tartar, Duncan, Shea and Ferrier,[1] and consisted of a hot-air engine to the side arm of which a box vial-holder was fastened. The machine gave approximately 300 shakes per minute, having "a vertical amplitude of two inches and a horizontal amplitude at one end only of the vial-holder of two inches."

Vials. The emulsions herein reported were prepared in 25 cc.vials which were always carefully washed, soaked in sulfuric acid-dichromate cleaning solution, rinsed and dried. They were stoppered with carefully cleaned, selected corks.

Transfer of Soap from Aqueous to "Oil" Phase

On repeating some experiments performed in this Laboratory in the summer of 1928 by Lothrop[2] and Pettengil[3] in which sodium stearate of 0.33 percent (approximately 0.01 normal) concentration was used, it was found that this solution gave water-in-oil emulsions (Briggs drop-dilution method)[4] within widely different phase-volume relationships when shaken with various organic liquids at room temperature. Lower concentrations, 0.002 and 0.003 normal, likewise produced water-in-oil emulsions when 1 cc of 0.2 normal sodium chloride was present. From the similarity of behavior of concentrated sodium stearate solutions and dilute solutions to which small amounts of the salt were added, it was apparent that the salt had a concentrating effect on certain constituents of the soap solution, probably the colloidal constituents. Stated differently, if the proper amounts of soap or salt are added to soap solutions of equal concentrations, a concentrating effect on the colloidal material is noticed in each. These experiments also revealed a very interesting and important property of concentrated solutions of the higher saturated sodium soaps when they were placed in contact with certain organic liquids, such as benzene, toluene, chlorobenzene, gasoline and carbon tetrachloride. When the aqueous phase had a sufficiently high initial concentration of these sodium soaps, there occurred a transfer of soap across the interface, into the organic liquid, in amounts depending on the original concentration and the organic liquid used. These aqueous soap solutions remain macroscopically clear only at temperatures above 45°-50° when not in contact with the non-aqueous phase and set to opaque fibrous gels when cooled to room temperature. This transfer phenomenon has been observed with thirteen liquids, immiscible with water; there are, no doubt, many more which will display similar behavior. The writers believe that this *important property of certain soaps has been entirely overlooked in the study of emulsions.*

The transferred soap appeared to be practically all in the form of the *gel*; only a trace was found on the evaporation of the benzene in contact with the

[1] Tartar, Duncan, Shea and Ferrier: J. Phys. Chem., 33, 435 (1929).

[2], [3] Master's theses yet unpublished.

[4] Briggs: J. Phys. Chem., 18, 34 (1914).

gel. The importance of the presence of the soap gel in the non-aqueous phase in systems which yielded only water-in-oil emulsions, was apparently increased by observations made later. When the gel was removed and the two phases shaken together, no emulsification took place. Large amounts of colloidal soap appeared in the non-aqueous phases of unshaken systems at equilibrium when sufficient sodium chloride had been added to salt-out the soap, e.g., sodium oleate; or when sufficient bivalent salt had been added to react with all the water-soluble soap present. Concentrated potassium stearate solutions (0.1 and 0.5 normal) in the presence of potassium chloride transferred an opaque, flaky material to the benzene phase. These systems, as did all others in which solid or colloidal material was shown to be present in the non-aqueous phase, yielded water-in-oil emulsions. These observations support the statement of Mead and McCoy[1] that for the production of a stable emulsion, there must be a "suitable emulsifying agent dissolved or dispersed in the continuous medium." At 25° only water-in-oil emulsions resulted when aqueous sodium stearate solutions whose concentrations exceeded 0.006 normal were shaken with benzene. This limiting concentration will probably vary for different organic liquids; transfer gelation has been observed to slight extent when solutions as low as 0.003 normal were left in contact with benzene for several hours.

The presence of sodium chloride (0.25 normal) in dilute sodium stearate solutions (0.002 normal) also induced the transfer of soap across the interfacial boundary, to form a "benzenated gel." The addition of the electrolyte was immediately followed by a profound change in the character of the interface of the unshaken systems. The height of the interfacial meniscus was greatly reduced and the boundary itself took on, at first, the appearance of a sheet of wrinkled tinfoil. Later tests showed this highly refracting film to be a benzenated gel. Qualitative tests proved that sodium hydroxide (1-normal) in the aqueous phase induced a rapid transfer of soap from a 0.002 normal sodium stearate solution to benzene. The presence of the sodium hydroxide of such strength eliminated the possibility of a transfer of free fatty acid or of acid soaps from the aqueous phase. Water-in-oil emulsions were produced when these systems were shaken.

Although no experimental proof of its existence is presented a micelle of different molecular orientation may be present. McBain[2] indicates that soap micelles which are "colloidally" soluble in water have the hydrocarbon ends of the soap molecules toward the interior of the aggregate. Under the conditions reported here might a rearrangement occur under the specific influence of the organic liquid making them soluble or solvatable in the non-aqueous phase? The benzene-soap gels are quite transparent, having an index of refraction not much different from that of benzene.

Quantitative determinations were made of the amount of soap transferred from aqueous solutions of various concentrations. Sodium stearate

[1] Mead and McCoy; "Colloid Symposium Monograph," 4, 44 (1926).

[2] McBain: "The Study of Soap Solutions" in Bogue: "Colloidal Behavior," 410 (1924).

and sodium palmitate solutions made by dissolving the pure soaps in warm water were placed in contact with equal volumes of benzene, until the lower aqueous layers seemed practically clear (usually allowed to stand 12-16 hours). The aqueous layers were then removed by pipet, whereupon the benzene-soap gel and excess benzene were quantitatively transferred to crucibles. After the benzene had been evaporated on the hot plate, the soaps were ignited to the alkali carbonate and weighed. The results given in Table I for sodium stearate and benzene at 25° are the mean of duplicate determinations, using in each case 25 cc. of the soap solution. Results for sodium palmitate are for a single determination.

TABLE I

Transfer of Sodium Stearate and Sodium Palmitate from Water to Benzene at 25°

Soap	Initial Conc. (N)	Total Soap (g.)	Transferred Soap (g.)	Diff. (g.)	Per cent Transfer
NaSt	0.005	0.0383	0.0211	0.0172	55.3
	0.010	0.0765	0.0611	0.0154	80.3
	0.020	0.1530	0.1384	0.0146	90.5
	0.030	0.2295	0.2115	0.0180	92.2
NaPa	0.005	0.0348	0.0153	0.0195	44.0
	0.010	0.0696	0.0563	0.0131	81.3
	0.020	0.1391	0.1247	0.0144	89.7
	0.030	0.2087	0.2055*	0.0032	98.2*

*Some aqueous phase enmeshed in gel probably explains high values.

These data show that the amount of soap remaining in the aqueous phase is constant, within experimental error, and perhaps roughly corresponds to the solubility of the sodium soaps in water saturated with benzene. The slight opacity of the aqueous layers, indicated, however, that part of the remaining soap was in colloidal suspension, possibly as acid soap[1] due to some hydrolysis of the resulting dilute soap solutions. The transfer isotherms are given in Fig. 1.

Although no extensive study of extraction of soaps from water by organic liquids was undertaken, some of the values reported above were checked by a method wherein precautions were taken to avoid the presence of carbon dioxide and slight temperature variations, and which permitted a rough estimate of the amount of free fatty acid in the benzene phase. Sodium stearate solutions, 0.01 and 0.02 normal, were placed in contact with benzene in sealed Pyrex flasks. These systems were gently rocked in a thermostat at 25° for 48 hours. The necks of the flasks were then cut off and the phases separated as before. After the benzene had been completely evaporated from the gels, the gels were dissolved in 50 cc. portions of neutralized ethyl

[1] McBain and Taylor: Z. physik Chem., 76, 179 (1911); McBain and Stewart: J. Chem. Soc., 1927, 1392.

alcohol (95 per cent) and the free fatty acid was titrated with sodium hydroxide, 0.0205 normal. The alcoholic solutions were then transferred to crucibles and evaporated to dryness. After correcting for the sodium content introduced by titration the amount of sodium stearate present in the gels could be calculated from the ignited carbonate residues. The results are given in Table II.

The data show that there was some error in this method of analysis because the sum of the sodium stearate in the benzene and of the sodium

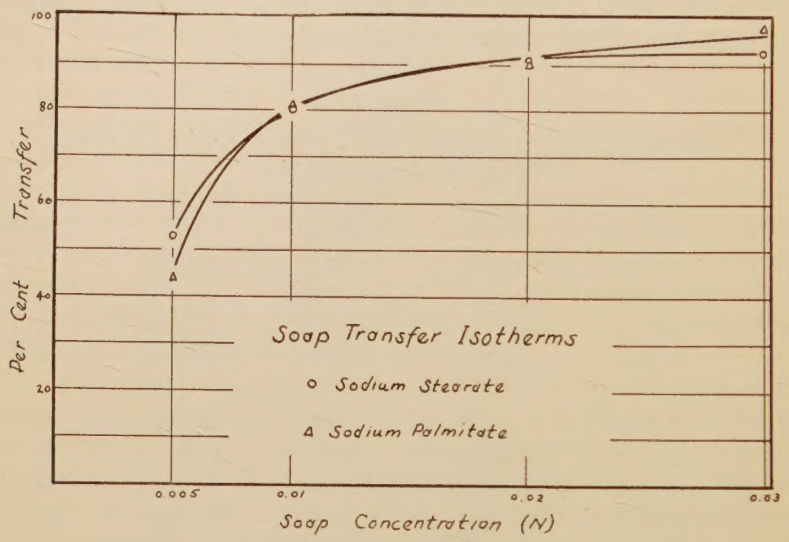

FIG. 1

TABLE II

Transfer of Sodium Stearate and Stearic Acid from Water to Benzene at 25°

Initial Conc. (N)	Total NaSt (g.)	HSt in Benzene	NaSt equiv. of HSt (g.)	NaSt in Bz (g.)	Per cent NaSt Transferred
0.01	0.0765	0.0127	0.0137	0.0654	85
0.02	0.1530	0.0118	0.0127	0.1442	94

stearate equivalent of the stearic acid present is greater than the amount of the sodium stearate initially present in the aqueous phase by about 3 per cent. The per cent sodium stearate transferred is correspondingly greater than that reported in Table I but the agreement is sufficiently close to establish the great preponderance of soap over the fatty acid in the benzenated gels.

Some information concerning the behavior of aqueous soap solutions in contact with benzene and p-xylene containing some of the corresponding fatty acid has been reported recently by McBain and his collaborators. McBain and Buckingham[1] state that at 90° there was a considerable quantity of palmitic acid extracted by p-xylene after the latter was rocked with solu-

[1] McBain and Buckingham: J. Chem. Soc., 1927, 2687.

tions of sodium palmitate. The addition of electrolytes was reported to lower the extractability of the acid from the soap solutions by the p-xylene. This was attributed to the reduction of the amount of molecular soap in solution, driving more of it into the colloidal state, which acts only as a reserve for molecular soap. The work reported here indicated, however, that at 25° electrolytes facilitated the transfer of soap itself to the non-aqueous phase.

The method of analysis of the p-xylene layer as outlined by McBain and Buckingham may be in serious error; the organic liquid was evaporated and the residue apparently considered as palmitic acid only. This may be true with p-xylene at 90° but it certainly is not true with benzene at 25°. In fact McBain and Buckingham[1] found that when the p-xylene contained palmitic acid in high concentrations that the residue weighed more than the total palmitic acid content, indicating that some sodium palmitate had also been extracted. This statement alone throws sufficient doubt on the assumption that the residues in the other cases were totally fatty acids.

McBain and Eaton[1] found that at 25° "sodium laurate is distinctly more extractable than potassium laurate." The work in this laboratory showed that sodium stearate was transferred easily to benzene, whereas potassium stearate fails to exhibit the property of transferred gelation even at 0.50 normal concentration.

Previous investigators of alkali soap emulsion systems have taken no account of the distribution of the soap between the two phases.[2] There are, however, a few scattered reports dealing with phenomena which bear directly on the above observations. No reference to a colloidal transfer of soap under similar conditions has been found in the literature but the existence of alkali soap gels in non-aqueous liquids has been previously observed.

The influence of a second liquid upon the formation of alkali soap gels in such liquids as turpentine, paraffin oil and benzene has been noted by Holmes and Maxson.[3] Since the present work was started Weicherz[4] reported that small quantities of phenol, the alcohols and water promote the solubility of alkali soaps in hydrocarbons and that at high soap concentrations water-in-oil emulsions are formed, reversing to oil-in-water on lowering the concentration. A somewhat similar concentration effect was reported by Harkins and Beeman.[5] They found that "a water-in-oil emulsion was produced by dissolving a large amount of soap in the oil and beating this up with water. This inverted to the ordinary oil-in-water type on the addition of more water." This change was no doubt induced by at least partial transfer of soap to the aqueous phase, or to the displacement of the equilibrium between the opposing emulsification tendencies, that stabilizing the oil-in-water type finally being

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[1] McBain and Eaton: J. Chem. Soc., 1928,

[2] Bancroft: J. Phys. Chem., **16**, 746 (1912), suggested that the reason Robertson: Kolloid-Z., **7**, 7 (1910) obtained both types of emulsions with olive oil and sodium oleate, and only one type when benzene or kerosene replaced olive oil, was the solubility of the soap in high olive oil concentrations and its insolubility in benzene and kerosene.

[3] Holmes and Maxson; "Colloid Symposium Monograph," **5**, 287 (1927).

[4] Weicherz: Naturwissenschaften, **16**, 654 (1928).

[5] Harkins and Beeman: Proc. Nat. Acad. Sci., **11**, 631 (1925).

in the ascendence. Fischer and Hooker[1] state that sodium stearate stabilizes water-in-oil emulsions but do not say, however, that the type depends in any way upon the concentration.

Mead and McCoy[2] made the observation that if an oil-in-water emulsion stabilized with sodium oleate were broken by sodium chloride and allowed to stand, some of the soap dissolved in the oil. If then the whole system were restirred vigorously, a water-in-oil emulsion resulted. This emulsion could be reversed by the addition of water and agitation. The latter behavior was undoubtedly due to the solution of more sodium oleate by water, since the salting-out effect of the sodium chloride was reduced by dilution. The parallelism between soap solutions of high concentrations and more dilute solutions to which electrolytes have been added is mentioned by McBain[3] in connection with viscosity of soap solutions. High viscosities may be obtained in either case but "are more quickly obtained by adding further quantities of the soap itself, rather than by adding equivalent amounts of the salts of alkali."

These isolated cases just mentioned confirm the results which have been obtained during the present investigation and indicate that the distribution of the soap between the two phases, regardless of the metal involved, is one type-determining factor which has hitherto been entirely overlooked in theorizing about emulsion type. The writers do not hold that the presence of a soap gel, per se, in the non-aqueous phase is a necessary condition for the production of water-in-oil emulsions at high soap concentrations. It is highly probable, however, that there is a redistribution of emulsifier during emulsification.

Influence of Temperature and Concentration of Soap Upon the Inversion of Emulsions

The experiments on the distribution of soap between the two phases suggested that the transfer from one phase to the other might be governed by the solubility of the soaps or their tendency to form solvates. Conditions which might be expected to influence these factors are, temperature, ratio of the volumes of the two phases within certain limits, the presence of electrolytes the specific nature of the organic liquid used and the state of aggregation of the soap in the aqueous phase. Qualitative experiments showed that the water-in-oil emulsions (aqueous phase-sodium-stearate-benzene) were very sensitive to increasing temperature and could be inverted to the oil-in-water type by heating the emulsion tube,[4] followed by gentle shaking. These oil-in-water emulsions could be changed back to water-in-oil systems if allowed to cool and stand for about 30 minutes. The observation was also made that the benzenated soap gel could be made to transfer back to the aqueous phase at approximately the temperature at which the inversion of the emulsions

[1] Fischer and Hooker: "Soaps and Proteins," 156 (1921).
[2] Mead and McCoy: "Colloid Symposium Monograph," 4, 44 (1926).
[3] McBain: Report Brit. Ass. Adv. Sci., 1920, 1-154 A.
[4] Reynolds: J. Chem. Soc., 119, 460 (1921).

took place. Water-in-oil emulsions produced by shaking benzene with dilute stearate solutions containing sodium chloride (0.2 normal) could likewise be inverted to oil-in-water emulsions by warming and shaking.

Perhaps a parenthetical description of these water-in-oil systems should be given. They were entirely similar to water-in-oil emulsions formed when bivalent soaps were used as stabilizers, excepting those stabilized by magnesium oleate. The water droplets were macroscopically visible and usually appeared as clear refractive spheres, probably surrounded by a transparent, plastic film, which prevented their coalescence. The large size of the droplets did not predetermine great instability, as is believed to be the case with oil-in-water emulsions. Some specimens have been standing for four months. Emulsions of the water-in-oil type with sodium stearate and sodium palmitate, especially in the presence of small amounts of sodium chloride, were very stable dispersions and fulfilled every requirement of ordinary emulsions except droplet size. The more concentrated the original soap solution the smaller the water droplets became. These facts argue that the emulsifying film was thicker or that the emulsifying agent functioned in larger aggregates in the water-in-oil than in the oil-in-water emulsions and consequently a given amount of soap occupied a smaller amount of interfacial surface in the stable water-in-oil types.

The appearance of the emulsions near the temperature of inversion changed markedly. Shaking produced a dual emulsion system, composed of large water droplets in which were suspended oil globules. The larger droplets were then white, due to the internal oil-in-water emulsions. Clowes[1] made a somewhat similar observation when inverting sodium oleate oil-in-water emulsions by the addition of calcium chloride. He states: "Beyond the critical point the emulsion consists principally of large drops of water surrounded by oil, which are characterized by the fact that they still contain numerous oil globules — —."

If solubility of the soap as controlled by temperature is an important factor in emulsion formation, emulsions with different soap concentrations should invert at different temperatures; i.e., the equilibrium existing between the two types of emulsifying units, if such there be, or at least between the two opposing functions of the soap present, should be displaced one way or the other through temperature changes.

Soap solutions of the various strengths examined were prepared by adding weighed amounts of pure soap to known volumes of hot water. Dilution of more concentrated solutions or progressive dilution through a series of concentrations was not sufficiently accurate. The method used is subject to small errors due to evaporation, slight volume differences, etc. The experiments were made in triplicate and the emulsions prepared by adding 5 cc of benzene to vials containing 5 cc of the hot soap solutions. The vials were quickly stoppered and allowed to cool to room temperature. They were then placed for 15 to 20 minutes in a thermostat at 5°. The cooled systems were

[1] Clowes: J. Phys. Chem., **20**, 407 (1916).

then given 5 minutes of vigorous shaking, meanwhile protecting against excessive radiation effects by having the box of the shaking machine well lined with cloths. Of course some radiation took place. After being examined as to type (Briggs' drop-dilution method) the emulsions were replaced in the thermostat at 7.5° for 15 to 20 minutes and again shaken and examined as before. The temperatures of inversion may be a degree or so too high because they represent the temperature of the thermostat. Examinations of type were made every 2.5 degrees until emulsions of all soap concentrations were

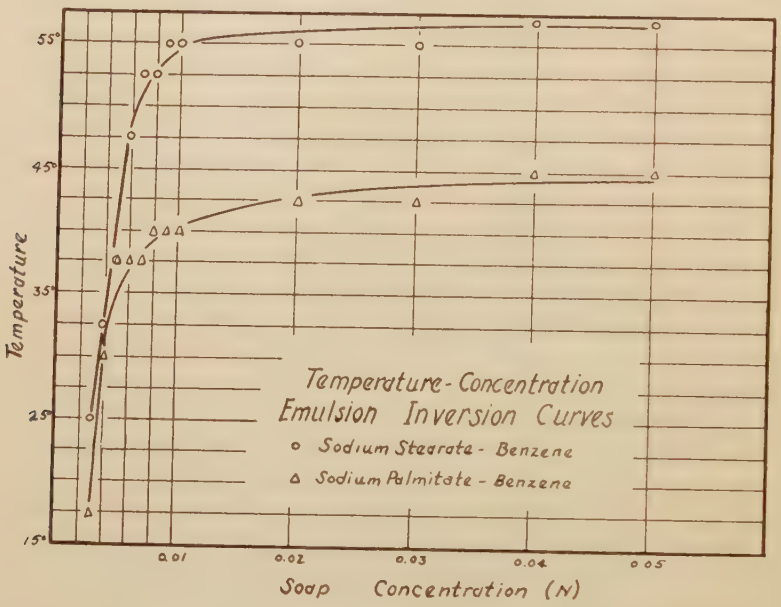

FIG. 2

inverted. The data are given in Table III and are shown graphically in Fig. 2.

The record of similar experiments with benzene-aqueous sodium palmitate systems is given in Table IV and graphed in Fig. 2.

The curves in Fig. 2 permit some very interesting conclusions. To the left and above the temperature-concentration curves the corresponding soap was unable to stabilize water-in-oil emulsions, whereas the area indicated under the curves produced only that type. The greater solubility of sodium palmitate over stearate in water is reflected in its lower "limiting temperature of inversion" at which the curves become approximately horizontal. These limiting temperatures are within a few degrees of the temperatures at which the soap solutions themselves lose their macroscopic colloidal appearance and apparently become clear solutions. The sharpness of this change is quite noticeable for most of the suspended soap disappears at once. In the region of the sharp breaks in the curves the points are a little uncertain. Both types, and especially the dual type, were present. Close to the inversion temperature a few hard shakes by hand proved more effective than machine shaking.

Table III

Temperatures of Inversion of Water-in-Oil Emulsions to Oil-in-Water Emulsions using Benzene and Aqueous Sodium Stearate at Various Concentrations

	Normality of Sodium Stearate x 10^3											
Temp.	3	4	5	6	7	8	9	10	20	30	40	50
15.0	WO	WO	WO	WO	WO	WO	WO	WO	WO	WO	WO	WO
17.5	WO	WO	WO	WO	WO	WO	WO	WO	WO	WO	WO	WO
20.0	WO	WO	WO	WO	WO	WO	WO	WO	WO	WO	WO	WO
22.5	*IP*	WO	WO	WO	WO	WO	WO	WO	WO	WO	WO	WO
25.0	OW′	WO	WO	WO	WO	WO	WO	WO	WO	WO	WO	WO
27.5	OW′	WO	WO	WO	WO	WO	WO	WO	WO	WO	WO	WO
30.0	OW′	*WO*	WO	WO	WO	WO	WO	WO	WO	WO	WO	WO
32.5	OW′	OW′	WO	WO	WO	WO	WO	WO	WO	WO	WO	WO
35.0	OW	OW′	*WO*	WO	WO	WO	WO	WO	WO	WO	WO	WO
37.5	OW	OW	′OW′	WO	WO	WO	WO	WO	WO	WO	WO	WO
40.0	OW	OW	OW′	WO	WO	WO	WO	WO	WO	WO	WO	WO
42.5	OW	OW	OW′	WO	WO	WO	WO	WO	WO	WO	WO	WO
45.0	OW	OW	OW′	*WO*	WO	WO	WO	WO	WO	WO	WO	WO
47.5	OW	OW	OW	′OW′	WO	WO	WO	WO	WO	WO	WO	WO
50.0	OW	OW	OW	OW′	*WO*	*WO*	WO	WO	WO	WO	WO	WO
52.5	OW	OW	OW	OW	′OW	OW′	*IP*	*IP*	*WO*	*WO*	WO	WO
55.0	OW	OW	OW	OW	OW	OW	′OW	OW	OW	OW′	*IP*	*IP*
56.5	OW	OW	OW	OW	OW	OW	OW	OW	OW	OW	′OW	OW

WO indicates water-in-oil emulsion.
OW indicates oil-in-water emulsion.
IP indicates inversion point, both types present.

Table IV

Temperatures of Inversion of Water-in-Oil Emulsions to Oil-in-Water Emulsions using Benzene and Aqueous Sodium Palmitate at Various Concentrations

	Normality of Sodium Palmitate x 10^3											
Temp.	3	4	5	6	7	8	9	10	20	30	40	50
15.0	*IP*	WO	WO	WO	WO	WO	WO	WO	WO	WO	WO	WO
17.5	OW′	WO	WO	WO	WO	WO	WO	WO	WO	WO	WO	WO
20.0	OW′	WO	WO	WO	WO	WO	WO	WO	WO	WO	WO	WO
22.5	OW′	WO	WO	WO	WO	WO	WO	WO	WO	WO	WO	WO
25.0	OW′	IP	WO	WO	WO	WO	WO	WO	WO	WO	WO	WO
27.5	OW′	*IP*	WO	WO	WO	WO	WO	WO	WO	WO	WO	WO
30.0	OW	′OW′	WO	WO	WO	WO	WO	WO	WO	WO	WO	WO
32.5	OW	OW′	WO	WO	WO	WO	WO	WO	WO	WO	WO	WO
35.0	OW	OW′	*IP*	*WO*	*WO*	WO	WO	WO	WO	WO	WO	WO
37.5	OW	OW	′OW	OW	OW′	*WO*	*WO*	*WO*	WO	WO	WO	WO
40.0	OW	OW	OW	OW	OW	′OW	OW	OW′	*WO*	*WO*	WO	WO
42.5	OW	OW	OW	OW	OW	OW	OW	OW	′OW	OW′	*WO*	*WO*
45.0	OW	OW	OW	OW	OW	OW	OW	OW	OW	OW	′OW	OW

Soap solution-benzene systems which were in equilibrium but had not been shaken sufficiently to produce emulsions, exhibited a return of the soap gel from the benzene to the aqueous phase, when the temperature was slowly increased. Almost complete transfer of the soap from the benzene to water took place 2 to 5 degrees higher than the inversion of the emulsion of corresponding soap concentration. This difference was probably due to the small interfacial areas in the unshaken systems as compared to the same systems after emulsification, making the transfer necessarily slower. Had it been possible to extend the interface without emulsifying the phases the return of the soap to the water probably would have been at the temperature of inversion to the oil-in-water type. At 60° the unshaken sodium stearate gels in benzene completely disappeared and the aqueous layer became very cloudy with colloidal material, leaving only a small amount of flaky substance floating near the benzene side of the interface.

The influence of subsequent lower temperatures on emulsions which had once undergone the water-in-oil to oil-in-water inversion was ascertained by placing the oil-in-water emulsions in a thermostat at 10° for 30 minutes and shaking them vigorously in the machine for 5 minutes. Without exception, water-in-oil emulsions were produced.

Tartar, Duncan, Shea and Ferrier[1] found that organic liquids, immiscible with water, differed in their susceptibility to emulsification by the same soap solution. This difference may be due to the respective transfer-distribution of the soap in the two phases. Although benzene, p-xylene, toluene, nitrobenzene, cyclohexane, chlorobenzene, bromobenzene, cumene, aniline, carbon tetrachloride, chloroform kerosene, gasoline and liquid petrolatum yielded water-in-oil emulsions when the amount of sodium palmitate was sufficient, their specific gelling powers towards the soap were widely different. There are also other properties of the organic liquids which undoubtedly have some effect, either on type directly or upon the stability of emulsions produced. Seifriz[2] reported that he obtained difference in type when light and heavy paraffin oils were shaken with water, wherein casein was used to stabilize the disperse systems; the lighter ones gave oil-in-water, the heavier ones, water-in-oil emulsions. There is a considerable change in the densities of the oils but the visicosities are also becoming greater as the density increases. The viscosity factor seems more apt to control the type of emulsion produced; the more viscous a liquid the greater difficulty to break it into droplets, and the slower the motion of a drop of a second liquid through the viscous one. So in the case of the heavier oils the water was more easily broken into droplets and these droplets were hindered in coalescing by the viscosity of the oil and the protective action of the casein. Stamm and Kraemer,[3] in a paper which gives an excellent criticism of the highly improbable "wedge theory" of emulsions, enumerate the mechanical and hydrodynamic factors of emulsion

[1] Tartar, Duncan, Shea and Ferrier: J. Phys. Chem., **33**, 435 (1929).
[2] Seifriz: J. Phys. Chem., **29**, 587 (1925).
[3] Stamm and Kraemer: J. Phys. Chem., **30**, 992 (1926).

systems which may be responsible for type determinations as "the particular mechanical treatment, character of the solid walls, volume composition, densities, viscosities, interfacial tensions and surface tensions (if a gas is present, as in shaking a partially filled bottle) of the liquids." Considering all these factors, generalities are dangerous and each emulsion system needs individual attention to produce the optimum conditions for stability.

Carbon tetrachloride, b. p. 75.8°-76.2°, was chosen as an "oil" of chemical and physical properties differing greatly from those of benzene. Its behavior in emulsions was very different from benzene. The results of attempts to determine accurately the temperature-concentration relations met with little success. In Table V are the data for one such attempt, when the conditions were similar to those obtaining in the aqueous sodium palmitate-benzene experiments.

TABLE V

Temperatures of Inversion of Water-in-Oil Emulsions to Oil-in-Water Emulsions using Carbon Tetrachloride and Aqueous Sodium Palmitate at Various Concentrations.

	Normality of Sodium Palmitate x 10^3											
Temp.	1	2	3	4	5	6	7	8	9	10	20	30
0.0	B	B	B	B	WO	WO	WO	WO	WO	WO	WO	WO
2.5	B	B	OW	OW	B	B	WO	WO	WO	WO	WO	WO
5.0	B	B	OW	OW	OW	OW	WO	WO	WO	WO	WO	WO
7.5	B	OW	OW	OW	OW	OW	WO	WO	WO	WO	WO	WO
10.0		OW	OW	OW	OW	OW	OW	OW	OW	WO	WO	WO
12.5		OW	OW	OW	OW	OW	OW	OW	OW	OW	WO	WO
15.0		OW	OW	OW	OW	OW	OW	OW	OW	OW	WO	WO
17.5		OW	OW	OW	OW	OW	OW	OW	OW	OW	WO	WO
22.5		OW	OW	OW	OW	OW	OW	OW	OW	OW	OW	WO
25.0		OW	OW	OW	OW	OW	OW	OW	OW	OW	OW	OW

B indicates broke; no lasting emulsion formed.

The data of Table V were far from satisfactory. In the first place, the water-in-oil emulsions were very poor; the droplet size was large and irregular and did not approach the stability of the same type when benzene, xylene, toluene, etc., were used. There was less uniformity among the three vials of each soap concentration; the table shows inversion when at least two of the three were inverted. Long periods of shaking were found to change the temperature necessary for inversion, which indicated slower progress in the attainment of equilibrium in the systems.

The ratio of the volumes of the two phases appeared in preliminary experiments to play a part in the length of shaking time necessary for inversion. Therefore experiments involving concentrations, phase-volume, ratio, and the length or amount of shaking as variables, were performed. In Table VI, which records the results of one experiment, the ratios are indicated by the capital letters at the heads of the columns; the ratio of the volume of the aqueous

TABLE VI

The Effects of Soap Concentration, Phase-Volume Ratio and Shaking Time on Carbon Tetrachloride-Aqueous Sodium Stearate Emulsions at 25°

Conc. V_{aq}/V_o Time	0.02 A	B	C	D	E	0.01 A	B	C	D	E	0.005 A	B	C	D	E
5	WO	WO	WO	WO	WO	OW	WO	B	WO	WO	OW	OW	OW	WO	WO
10	WO	WO	WO	WO	WO	OW	OW	B	WO	WO	OW	OW	OW	Oi	Oi
15	WO	OW	WO	WO	WO	OW	OW	OW	WO	WO	OW	OW	OW	Oi	Oi
20	OW	OW	WO	WO	WO	OW	OW	OW	WO	WO	OW	OW	OW	OW	Oi
25	OW	OW	WO	WO	WO	OW	OW	OW	WO	WO	OW	OW	OW	OW	Oi
35	OW	OW	OW	Oi	Oi	OW	OW	OW	Oi	Oi	OW	OW	OW	OW	Oi
45	OW	OW	OW	Oi	Oi	OW	OW	OW	Oi	Oi	OW	OW	OW	OW	Oi

TABLE VII

The Effects of Soap Concentration, Phase-Volume Ratio and Shaking Time on Benzene Aqueous Sodium Stearate Emulsions at 25°

Conc. V_{aq}/V_o Time	0.02 A	B	C	D	E	0.01 A	B	C	D	E	0.005 A	B	C	D	E
5	WO	WO	WO	WO	WO	IP	WO	WO	WO	WO	OW	WO	WO	WO	WO
10	WO	WO	WO	WO	WO	IP	WO	WO	WO	WO	OW	WO	WO	WO	WO
15	WO	WO	WO	WO	WO	IP	WO	WO	WO	WO	OW	WO	WO	WO	WO
20	WO	WO	WO	WO	WO	IP	WO	WO	WO	WO	OW	WO	WO	WO	WO
25	WO	WO	WO	WO	WO	IP	WO	WO	WO	WO	OW	WO	WO	WO	WO
30	WO	WO	WO	WO	WO	IP	WO	WO	WO	WO	OW	WO	WO	WO	WO
40	WO	WO	WO	WO	WO	IP	WO	WO	WO	WO	OW	WO	WO	WO	WO
50	WO	WO	WO	WO	WO	IP	WO	WO	WO	WO	OW	WO	WO	WO	WO
60	WO	WO	WO	WO	WO	IP	WO	WO	WO	WO	OW	WO	WO	WO	WO

phase to the volume of the oil phase (V_{aq}/V_o was 7.5 to 2.5 in A, 6 to 4 in B, 5 to 5 in C, 4 to 6 in D, and 2.5 to 7.5 in E. The notation "Oi" indicates oil-in-water emulsions but emulsification incomplete. The emulsions were shaken 5 minutes at a time with approximately 5 minutes rest between.

Preliminary experiments with benzene showed no such variation, even on much longer shaking. Table VIII, however, was prepared in order to make certain of this important difference between the two organic liquids. Table VIII was prepared to supplement the data of Table VII; 0.005 normal sodium stearate was used through a wider range of phase volume ratios. Experiments on other organic liquids would no doubt show at least quantitative differences in these properties of emulsions. Because of the pronounced gelling of sodium soaps in benzene and the ease of examining its relation to emulsion type-determination, these higher saturated sodium soaps have been studied more extensively than the lower soaps of the same metal or the corresponding potassium soaps.

TABLE VIII

The Effects of Phase-Volume Ratio and Shaking Time on Benzene-Aqueous Sodium Stearate Emulsions at 25°

$\frac{V_{aq}}{V_o}$ Time	$\frac{9.5}{0.5}$	$\frac{7.5}{2.5}$	$\frac{5.0}{5.0}$	$\frac{2.5}{7.5}$	$\frac{0.5}{9.5}$
5	OW	OW	WO	WO	WO
10	OW	OW	WO	WO	WO
15	OW	OW	WO	WO	WO
20	OW	OW	WO	WO	WO
25	OW	OW	WO	WO	WO

Emulsions stabilized with Bivalent Soaps

Comparatively little experimental work has been done on water-in-oil emulsions stabilized by soaps of the bivalent and trivalent metals. Newman[1] tried to stabilize water-in-benzene emulsions through the use of the oleates of magnesium, zinc, nickel and calcium and found that only magnesium oleate gave satisfactory results. Mead and McCoy[2] studied some of the oil-soluble emulsifying agents but their results contributed but little to the general knowledge of water-in-oil emulsions. In the study of the inversion of oil-in-water emulsions stabilized with univalent soaps through the action of the salts of the bivalent and trivalent metals, no cognizance has been taken of the effect of the univalent salts produced by metathesis, on the stability of the resulting emulsion systems. These emulsions are usually unstable.

The present experimental work indicated that distribution of bivalent soaps between phases is also a governing factor of emulsion type. When dilute aqueous solutions of magnesium heptylate, magnesium caprylate, magnesium caproate or calcium valerate were shaken with equal volumes of benzene,

[1] Newman: J. Phys. Chem., **18**, 45 (1914).

[2] Mead and McCoy: "Colloid Symposium Monograph," **4**, 44 (1926).

oil-in-water emulsions were formed. These emulsions had different degrees of stability but persisted in some cases for 2 to 4 hours, which is longer than many water-in-oil emulsions last, whether they are made by inversion of a univalent soap emulsion or by the presence of the bivalent soap in the oil phase originally.

Water-in-oil emulsions were prepared through the use of more concentrated bivalent soap solutions in which solid or colloidal soap was present. These systems often broke completely within 10 or 15 minutes, the soap being largely precipitated in the non-aqueous phase. Inversion to the oil-in-water type was invariably accomplished by the addition of small amounts of water, followed by vigorous shaking. The addition of more benzene was found to favor the formation of water-in-oil emulsions.

Because of the small amounts of these soaps available, thorough quantitative studies on these reversal phenomena were impossible, but the qualitative observations support the belief that increasing the relative amount of soap in one of the phases tends to make that phase the dispersion medium of the emulsion. This may be accomplished by increasing the volume of such a phase (which changes the concentration of the soap in the other phase) or by a temperature change which favors the passage of the soap to that phase.

The oleates of calcium and magnesium are fairly easily dissolved by warm benzene; barium oleate seems to be the least soluble. When benzene solutions of these bivalent oleates were shaken with water the influence of the phase-volume relationship was very noticeable; the phase having the greater volume usually became the continuous one. A noteworthy observation was made when 5 cc of any of these oleate solutions in benzene were shaken with an equal volume of water. Gentle or moderate shaking invariably produced emulsions of the water-in-oil type while violent shakes by hand produced inversion to the oil-in-water type. The latter were the more stable, sometimes lasting for several hours, while the water-in-oil dispersions usually broke within 10 or 15 minutes. After breaking, the type of emulsion produced on subsequent shaking seemed entirely dependent on the mechanical treatment. The phenomenon was not greatly affected by temperature changes; oil-in-water emulsions seemed somewhat more easily produced at 60° than at 15°. Concentration of the soap in the benzene seemed to play a small part, because solutions of calcium oleate of 0.001, 0.005, 0.01, 0.02 and 0.05 volume normality were equally susceptible to the differences in methods of shaking.

A fact which apparently supports the colloidal or solid film theory of water-in-oil emulsifiers was observed during the experiments just reported. Without exception, flaky material was present in the benzene phase after the bivalent soap emulsions had broken. All that is needed to produce this phenomenon is to put *water in contact* with the benzene solution; shaking appeared only to hasten the precipitation. Dry benzene solutions of these soaps remained clear. The separation of the soap when the benzene became saturated or moist with water throws doubt on the assumption that solution of the bivalent soap in benzene is the cause for the inversion of oil-in-water to water-in-oil emulsions by electrolytes. There is no doubt, however, that the

precipitated or flocculent bivalent soap is more easily wetted by benzene than by water. The above objection obtains whether the bivalent soap is dissolved in the "oil" to start with or is produced through metathesis in an emulsion system. Water-in-oil emulsions have generally been reported as being unstable. This instability can be understood if fairly in-elastic, solid films, or films of little cohesive strength are responsible for the temporary emulsification. Electrolytes present in inverted emulsion systems would be expected to affect the permanency of colloidal films.

Contrary to current ideas, the oleates of calcium, magnesium and barium were found to be sufficiently soluble in water to stabilize oil-in-water emulsions.[1] These pure bivalent oleates were shaken in pyrex bottles with dis-

TABLE IX

Influence of Phase-Volume on Emulsion Type of Benzene Bivalent Oleate Systems at 25°

Soap	Phase Volume Ratio, V_{aq}/V_o		
	8/2	5/5	2/8
$MgOl_2$	OW	OW	Broke
$CaOl_2$	OW	OW_x	Broke
$BaOl_2$	OW	OW_x	Broke

x—required subsequent shaking by hand.

TABLE X

Influence of Phase-Volume on Emulsion Type of Benzene Bivalent Oleate Systems at 25°

Soap	Phase Volume Ratio, V_{aq}/V_o		
	8/2	5/5	2/8
$MgOl_2$	OW	WO_x	WO_x
$CaOl_2$	OW_z	$OW^{\perp}$	Broke
$BaOl_2$	OW#	$OW^{\perp}$	Broke

z—separated into 2 layers after 20 minutes.
#—Separated into 2 layers after 10 or 12 minutes.
⊥—required vigorous shaking by hand.
x—WO emulsions using $MgOl_2$ were the only ones of this type produced in this work which had the apparent droplet size and creaminess of OW emulsions, which confirms the experience of Newman[2] and of Parsons and Wilson.[3]

tilled water for 30 hours at 25°, after filtration the solutions were preserved in glass-stoppered pyrex bottles. Surprisingly good oil-in-water emulsions were produced when organic liquids were added in three 2 cc portions to 10 cc of these saturated aqueous solutions. The systems were shaken after each addition of the oil phase. With this phase-volume ratio, oil-in-water emulsions were formed with the following "oils" when they were shaken with aqueous

[1] Bhatnagar: J. Chem. Soc., **117**, 542 (1920) obtained oil-in-water emulsions when olive oil was shaken with calcium hydroxide solutions of less than 0.002 normality; the type was found to depend in part on the phase-volume ratio.

[2] Newman: J. Phys. Chem., **18**, 34 (1914).

[3] Parsons and Wilson: J. Ind. Eng. Chem., **13**, 1116 (1921).

solutions of these bivalent oleates: carbon tetrachloride, chloroform, aniline, nitrobenzene, kerosene, benzene and toluene. The "oils" listed above are in the order of increasing stability of the emulsions.

The phase-volume influence on such systems was studied. The two phases of the respective systems were in contact 16 hours before they were given vigorous machine shaking for 15 minutes. The results are reported in Table IX.

Benzene solutions of these bivalent oleates (of unknown concentration) were prepared and placed in contact with distilled water for 16 hours. The phase volume influence was again ascertained, as before. The data are recorded in Table X.

The effect of electrolytes on the efficiency as emulsifiers of the oleates of calcium, magnesium and barium was investigated. Five cc of the saturated aqueous solutions of these soaps were shaken with 2 cc of benzene (which phase-volume relationship had been found to yield oil-in-water emulsions) and 1 cc of 1-normal electrolyte added. The time required for the first evidence of the separation of the emulsions into two phases was taken as an arbitrary standard of stability. The systems were given 5 violent shakes by hand and the time taken with a stop-watch. The results presented in Table XI are the means of 5 determinations.

TABLE XI

Effects of Uni- and Bivalent Chlorides on Emulsions of Benzene stabilized by Some Bivalent Oleates

Salt Added / Soap	None	NaCl	$BaCl_2$	$CaCl_2$	$MgCl_2$
			Time in Seconds		
$BaOl_2$	49	11	9	—	—
$CaOl_2$	67	22	—	12	—
$MgOl_2$	63	—	—	—	14

	cc 1−n NaCl		
	1	2	3
Time	60	53	33

The data of Table XI prove the necessity of considering the presence of electrolytes when studying emulsion stability. Those emulsions containing no electrolyte persisted for more than an hour, while the others lasted less than 2 minutes. Regardless of the condition of the emulsifying agent in the oil-in-water emulsions, the results show them to be extremely sensitive to electrolytes. Such sensitivity is to be expected if the original emulsifying film is a colloid; the salts precipitate the colloids and the emulsions break. Water-in-oil emulsions were not formed after the addition of electrolytes in the systems just reported, because of the deficiency of suitable emulsifying material for this type of emulsion.

The above findings with bivalent soaps as emulsifying agents indicate the fallacy of drawing conclusions concerning their specific functions *when electroyltes of any type are present in the system.* The presence of solid or colloidal material in the non-aqueous phases whenever water-in-oil emulsions

are produced, supports the statement of Briggs,[1] that "in every case, investigation has shown that the apparently soluble emulsifier is in colloidal suspension in the outside phase of the emulsion and therefore constitutes a third phase in the system, exactly as a solid emulsifier can be seen to constitute a third phase in such systems. Furthermore, it is accepted by nearly everybody that the globules of liquids in all ordinary emulsions are invariably coated by some kind of film or pellicle which tends to prevent coalescence, and that this film or pellicle is present whether the emulsifier is apparently soluble or consists of a finely divided solid. In view of the vast majority of experimental evidence, it seems safe to assume that the presence of a film of emulsifying agent is absolutely essential to the existence of all ordinary emulsions."

The data presented here on the use of both univalent and bivalent soaps in the stabilization of either type of emulsion emphatically contradicts the oriented wedge theory[2] of emulsions. It neither contradicts nor supports the idea of orientation of the soap molecules at the dispersion interfaces but it does not allow the geometrical relations of the soap molecule to be the determining factor in the curvature of such interfaces. Such geometrical relations cannot, therefore be the type-determining factor of emulsions stabilized with soaps. As will be shown later, the emulsifying power of soaps probably depends on their colloidal properties; the effective colloidal properties of the solution are increased by adsorption of the surface-active colloid into the liquid-liquid interface. The result is a film or *third phase* appearing in the system which is capable of preventing coalescence of droplets, formed by mechanical means, and which appears to be in no way dependent on the relative diameters of the two ends of the soap molecule.

The Effects of Electrolytes on Emulsions

(a). *Inversion.* Robertson,[3] Newman,[4] Briggs and Schmidt,[5] Clowes,[6] Bhatnagar,[7] Parsons and Wilson,[8] and Ghosh and Dhar[9] have inverted stable oil-in-water emulsions, stabilized by water-soluble alkali soaps, to the more unstable water-in-oil systems by the addition of salts of the bi- and trivalent metals. The work of Tartar, Duncan, Shea and Ferrier[10] has demonstrated a similar inversion in the case of certain sodium soaps, when sodium chloride is present in sufficient concentration. The mechanism of the reversal of phases

[1] Briggs: J. Ind. Eng. Chem., **13**, 1008 (1921).

[2] Harkins, Davies and Clark: J. Am. Chem. Soc., **39**, 586 (1917); Harkins and Keith: Science, **59**, 463 (1924); Harkins and Beeman: Proc. Nat. Acad. Sci., **11**, 631 (1925); Finkle, Draper and Hildebrand: J. Am. Chem. Soc., **45**, 2780 (1923); Langmuir: J. Am. Chem. Soc., **39**, 1848 (1917).

[3] Robertson: Kolloid-Z., **7**, 7 (1910).

[4] Newman: J. Phys. Chem., **18**, 34 (1914).

[5] Briggs and Schmidt: J. Phys. Chem., **19**, 478 (1915).

[6] Clowes: J. Phys. Chem., **20**, 407 (1916).

[7] Bhatnagar: J. Chem. Soc., **117**, 542 (1920); 542 (1920); **119**, 61 (1921).

[8] Parsons and Wilson: J. Ind. Eng. Chem., **13**, 1116 (1921).

[9] Ghosh and Dhar: J. Phys. Chem., **30**, 294 (1926).

[10] Tartar, Duncan, Shea and Ferrier: J. Phys. Chem., **33**, 435 (1929).

has received some speculative attention from various investigators but about all that can be said with certainty concerning the phenomenon is that it is accompanied in each instance by the appearance in the emulsion system of soap, whose solubility in water is very low.

The work of Clowes has received rather wide-spread attention and has been used as a basis for a large part of the present-day emulsion theory. It is lamentable that he employed materials such as olive oil, whose composition is variable, and that he relied upon the very uncertain method of producing the emulsifying soap by having in the olive oil "sufficient oleic acid to form soap with all the NaOH introduced into the aqueous phase." Results to be given shortly are in direct contradiction with those reported by Clowes and prove that his interpretation does not apply to all soap emulsion systems. The writers believe that Clowes was led to his erroneous conclusion by the use of oil and a method which were open to question.

The principal thesis of his paper[1] seems to be an attempt to show that the molecular "100 to 1" ratio of sodium chloride to calcium chloride in a so-called "antagonistic effect," noticed in certain physiological systems, is effective in the establishment of "emulsion equilibrium." This antagonism is said to be manifested in the permeability of the soap film to water, sodium chloride making the emulsifying film more permeable to water and thus exerting a "destructive" effect on the film, while calcium chloride has a "protective" influence since it renders the film less permeable to water. It is proposed that these opposing influences are not the result of an antagonism between the cations involved but to "a balance between cations on the one hand, and anions on the other, adsorbed on or reacting with the soaps or other colloidal constituents of the surface films or membranes. It simply happens that, in the case of $CaCl_2$, the cation Ca is far more readily adsorbed than the anion Cl, while, in the case of NaCl, the anion Cl is somewhat more readily adsorbed than the cation Na." Although Clowes mentioned, in the above quotation, the possibility of the electrolyte "reacting with soaps—" the reported opposing influences of the two salts are subsequently entirely dealt with from the standpoint of preferential adsorption of the various ions by the soap film. Clowes found that sodium chloride in concentrations up to 0.1 M "promotes the adsorption of negative ions on the soap particles and consequently promotes the dispersion of soap in water, thus facilitating the formation of emulsions of oil dispersed in water." Of course what he meant to say, was, that since sodium chloride facilitated the formation of oil-in-water emulsions, it must be that negative ions were adsorbed on the soap particles

If such a thing as "emulsion equilibrium" exists in systems containing both sodium and calcium chlorides, the condition should be reached by the addition of either salt to systems containing the other; and if the balancing ratio of 100 molecules of sodium chloride to 1 molecule of calcium chloride, as found by Clowes, is due to an ion-adsorption equilibrium, it should be present in all emulsion systems containing sodium oleate, sodium chloride

[1] Clowes: J. Phys. Chem., 20, 407 (1916).

and calcium chloride. Experiments were outlined and performed to test the validity of these points.

The data of Table XII show the type of emulsions produced when solutions of calcium chloride of various concentrations were added to oil-in-water emulsions whose aqueous phases contained sodium oleate of 0.01 normal concentration and sodium chloride of various concentrations, and whose dispersed oil phase was benzene. The final volume of each phase was 6 cc, the various components of the systems being added from burets. The concentrations indicated in the table are for the final aqueous phase and are expressed as volume normalities. Sodium oleate solution, water, sodium chloride solution and benzene were introduced into the vials in the order named, prior to emulsification. The calcium chloride solutions were then added.

TABLE XII

Effects of Sodium Chloride and Calcium Chloride on Emulsions of Benzene in Aqueous Sodium Oleate at 25°

NaCl (Normality)	$CaCl_2$ (Normality)						
	0.0	0.0001	0.0005	0.001	0.005	0.01	0.0125
0.0	OW	OW	OW	OW	OW_x	WO	WO
0.05	OW	OW	OW	OW	OW_x	WO	WO
0.10	OW	OW	OW	OW	OW	WO_z	WO
0.15	OW	OW	OW	OW	OW	WO_z	WO_z

All WO emulsions were very unstable.

The presence of sodium chloride was without noticeable influence on the inverting action of calcium chloride. The importance of the equivalent concentrations of sodium oleate and calcium chloride at the inversion points should be emphasized. If Clowes' 100 to 1 molecular ratio is of general importance, breaking of the oil-in-water emulsions certainly should have taken place at the concentrations marked (x) and there should have been no inversion at the concentrations marked (z). There should have been no emulsion formed at calcium chloride concentration 0.005 normal when no sodium chloride was present, if sodium and calcium oleates have equal but opposite emulsifying properties; they were in equivalent proportions in that system. After standing 24 hours the oil-in-water emulsions had separated into 2 layers, the emulsion above an aqueous layer. With increasing calcium chloride concentration, the lower aqueous layers became increasingly turbid. The inverted systems broke in less than 30 minutes and on standing, the benzene layer became clear, except for flocculent material near the interface. The last emulsions of the last two columns separated into two practically clear layers, with considerable precipitated soap at the interfae, showing *an additive rather than antagonistic effect* of sodium chloride to calcium chloride.

The interval between the concentrations of calcium chloride 0.005 to 0.01 normal was included in the experiment recorded in Table XIII. All other conditions were maintained as described for the data of Table XII.

TABLE XIII

Effects of Sodium Chloride and Calcium Chloride on Emulsions of Benzene in Aqueous Sodium Oleate at 25°

NaCl (Normality)	$CaCl_2$ (Normality) 0.006	0.007	0.008	0.009
0.0	OW	OW	OW_x	OW_z
0.05	OW	OW	OW_x	OW_z
0.10	OW	OW	OW_x	OW_z
0.15	OW	OW_x	OW_x	OW_z

x—separated into 3 layers; benzene, oil-in-water emulsion, water.
z—gentle shaking produced WO but when these were broken and the emulsions were given violent shaking by hand, OW were produced, which separated into 3 layers after 10 minutes.

Table XIII shows evidence of an additive effect of the two chlorides on the breaking of these emulsions. The last system of the first column and the last two of the second column were practically identical with the first two of the third column after standing 4 days. The calcium chloride introduced apparently converted its equivalent of sodium oleate into calcium oleate, while the sodium chloride in 0.10 and 0.15 normal concentrations was beginning to exert its salting-out effect on the remaining sodium oleate. The complete salting-out of soaps occurs at a still higher sodium chloride concentration and is apparently independent of the concentration of the soap.[1]

TABLE XIV

Effects of Sodium Chloride and Calcium Chloride on Emulsions of Benzene in Aqueous Sodium Oleate at 25°

NaCl (Normality)	$CaCl_2$ (Normality) 0.001	0.005	0.010	0.0125
0.0	OW	OW	WO	WO
0.05	OW	OW	WO	WO
0.10	OW	OW	WO	Broke
0.15	OW	OW	WO	Broke

All WO emulsions were unstable.

Experiments were performed in which the order of addition of the sodium and calcium chlorides were interchanged; i.e., the calcium chloride was added prior to emulsification, the sodium chloride afterward. Only the concentrations of calcium chloride 0.005 and 0.01 normal were investigated because from the previous experiments one was below, the other approximately at, the critical concentration for this system. The concentrations and conditions of the experiment were of the standard type described for Table XII. Good loi-in-water emulsions were produced at the lower calcium chloride concentration even before the addition of sodium chloride, whereas unstable water-in-oil dispersions resulted from the use of 0.1 normal calcium chloride, on which the addition of sodium chloride had no apparent effect.

[1] McBain and Pitter: J. Chem. Soc., **1926**, 893; Parsons and Wilson: J Ind. Eng. Chem., **13**, 1116 (1921).

One set of experiments was performed in which all components of the emulsion systems were placed in the vials before emulsification by shaking was accomplished, other conditions remaining as before. The results are reproduced in Table XIV.

The only effect of the presence of sodium chloride on the action of calcium chloride in the above systems was noticed before emulsification. The calcium oleate precipitates in those tubes containing sodium chloride, were much more curdy than the precipitates in the absence of the sodium salt. From the similarity of Tables XII and XIV this difference was without consequence.

The additive properties of sodium and calcium chlorides on the breaking and inverting of emulsions stabilized with sodium oleate was even more pronounced when carbon tetrachloride was used in place of benzene. Table XV records the results of an experiment in which calcium chloride was added after the carbon tetrachloride had been emulsified in the aqueous phase which contained both oleate and chloride of sodium. Before emulsification, a pronounced precipitating effect of sodium oleate by carbon tetrachloride was noticed in all the systems containing sodium chloride in 0.15 normal concentration.

TABLE XV

Effects of Sodium Chloride and Calcium Chloride on Emulsions of Carbon Tetrachloride in Aqueous Sodium Oleate at 25°

NaCl (Normality)	$CaCl_2$ (Normality)					
	0.005	0.006	0.007	0.008	0.009	0.010
0.0	OW	OW	OW	IP	WO	WO
0.05	OW	OW	IP	IP	WO	WO
0.10	OW	OW_x	IP	IP	WO	WO
0.15	OW+	WO	WO	WO	WO	WO_z

x—after 1/2 hour showed signs of IP.
+—after 1-1/2 hour showed signs of IP.
z—separated into 3 layers after 2 hours; showed precipitating effect of NaCl.

Time is a factor in the breaking of these emulsions. After 2 days the inversion point moves toward the left of the table; i.e., after 2 days the last system of the first column, and the second and third of the second column were clearly at the inversion point (IP), while the third systems of the third and fourth columns had broken to yield water-in-oil emulsions on shaking.

Interchanging the order of addition the sodium and calcium chlorides seemed to have a slight effect on the stability of the emulsions produced, but the effect was different from what might be expected. The precipitating effect of sodium chloride on these systems was more retarded than in the previous case. Table XVI shows the condition of the systems after 2 hours standing. Good oil-in-water emulsions were prepared in the presence of calcium chloride up to and including concentrations 0.008 normal; above 0.008 normal, unstable water-in-oil systems were produced. The emulsions stood 16 hours before the sodium chloride solutions were added.

TABLE XVI

Effects of Sodium Chloride and Calcium Chloride on Emulsions of Carbon Tetrachloride in Aqueous Sodium Oleate at 25°

NaCl (Normality)	$CaCl_2$ (Normality)					
	0.005	0.006	0.007	0.008	0.009	0.010
0.0	OW	OW	OW	IP	WO	WO
0.05	OW	OW	OW_x	IP	WO	WO
0.10	OW	OW_x	OW_x	IP	WO	WO
0.15	OW_x	OW_x	IP_z	IP	WO	WO

x—at IP after 5-10 days.
z—WO, after 5 days.

The conditions of the respective emulsions of Tables XV and XVI were practically identical throughout, after 10 days.

Although the salting-out of potassium soaps by potassium salts is more difficult than with corresponding sodium systems, potassium chloride did have a slight additive effect to that of barium chloride on emulsions of benzene in aqueous potassium oleate. In Table XVII are given the types of emulsions resulting when barium chloride solutions of various strengths were added to emulsion systems containing different potassium chloride concentrations. The final potassium oleate concentration was 0.01 normal.

TABLE XVII

Effects of Potassium Chloride and Barium Chloride on Emulsions of Benzene in Aqueous Potassium Oleate at 25°

KCl (Normality)	$BaCl_2$ (Normality)						
	0.0	0.005	0.006	0.007	0.008	0.009	0.010
0.0	OW	OW	OW	OW	IP	WO	WO
0.1	OW	OW	OW	OW	IP	WO	WO
0.2	OW	OW	OW	OW	IP	WO	WO
0.3	OW	OW	OW	OW	IP	WO	WO
0.4	OW	OW	OW	IP	IP	WO	WO
0.5	OW	OW	OW	IP	IP	WO	WO

The experiments recorded in Tables XII to XIV strip Clowes' so-called "emulsion equilibrium" of its appearance of generality and suggest that the explanation of the phenomenon he observed is to be found in the uncertainties of his complex emulsion systems. The instability of the systems reported here as the equivalent concentration of calcium chloride approaches that of sodium oleate, and the breaking and inverting of the systems when these concentrations become equal, regardless of the presence of sodium chloride, demonstrate that the complete conversion of the water-soluble soap present to one much less soluble in water, is the underlying cause of the breaking and inverting of these emulsions. The present work confirms the results obtained by Parsons and Wilson[1] who found that the determining factor in inverting

[1] Parsons and Wilson: J. Ind. Eng. Chem., 13, 1116 (1921).

Nujol-sodium oleate oil-in-water emulsions by magnesium salts was the ratio of the *equivalents* of magnesium to sodium. The ions "reacting with the soaps" rather than those "adsorbed on" thus appear to be the true inversion agents.

(b). *Interfacial Tension.* Since the work of Quincke[1] and Donnan[2] the importance of low interfacial tension between emulsion phases to the ease of emulsification and the stability of the resulting emulsions, has been realized. It is without the province of this paper to review the literature (which is quite abundant) on this phase of the emulsion problem, but the reader is referred to Clayton's[3] résumé. The determination of interfacial tensions of some emulsion systems which had suffered inversion through the influence of electrolytes was the extent of the work to be herein reported.

Although sodium chloride is negatively adsorbed at the air-water interface, causing an increase in the surface tension of the liquid against air, and although it causes a slight increase in the interfacial tension of water against benzene,[4] its presence in solution of sodium oleate greatly lowers the interfacial tension against benzene.[5] Clowes[6] found that sodium chloride in the alkali solutions which he used, greatly increased the drop number against olive oil, which indicated a decrease in interfacial tension. Since the work of Tartar, Duncan, Shea and Ferrier[7] has shown the inverting action of sodium chloride in certain instances, one of their reproducible systems was chosen for study of the interfacial tension. One of Bhatnagar's[8] systems was duplicated and the interfacial tension change produced by the addition of barium nitrate to sodium oleate solutions was likewise studied, while a new system of potassium stearate, potassium chloride and benzene was investigated.

An instrument patterned after that of Fahrenwald[9] was built. The scale was calibrated in grams and when using an interfacial tension blade of 2.13 centimeters in length, the readings of the instrument were accurate to 0.06 dyne. With this instrument the interfacial tension of mutually saturated benzene-water, was found to be 34.87 dynes at 25°. Harkins and Zollman[10] reported 35.00 dynes for the same tension at 20°, when they used the modified drop-weight method.

The equilibrium systems of aqueous sodium oleate, sodium chloride and benzene were prepared by overlaying 2 percent sodium oleate solutions with benzene and then adding aqueous sodium chloride to give the concentrations

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[1] Quincke: Wied. Ann., **35**, 589 (1888).
[2] Donnan: Z. physik. Chem., **31**, 42 (1899).
[3] Clayton: "Theory of Emulsions," 2d Ed., 63 (1928).
[4] Harkins and Humphrey: J. Am. Chem. Soc., **38**, 242 (1916).
[5] Harkins and Zollman: J. Am. Chem. Soc., **48**, 69 (1926).
[6] Clowes: J. Phys. Chem., **20**, 407 (1916).
[7] Tartar: Duncan, Shea and Ferrier: J. Phys. Chem., **33**, 435 (1929).
[8] Bhatnagar: J. Chem. Soc., **119**, 61 (1921).
[9] Fahrenwald: J. Optical Soc. America, **6**, 722 (1922).
[10] Harkins and Zollman: J. Am. Chem. Soc., **48**, 69 (1926).

indicated in Table XVIII and to reduce the sodium oleate concentrations to 1 percent. The systems were brought to equilibrium by rotating them gently by hand at intervals for 16 hours. At the end of that time, clear samples from each of the immiscible layers were pipetted off and the interfacial tensions measured at 23°. Figure 3 shows graphically the interfacial tension changes.

All the interfacial tension values reported in Table XVIII are the means of at least 5 determinations except the third, which is for 4 determinations. When making the measurements on the third system, considerable spontaneous emulsification took place, which interfered with the accuracy of the measurements. Simultaneous emulsification tests showed that if none of

TABLE XVIII

Interfacial Tension of Benzene-Sodium Oleate Equilibrium Systems containing Various Amounts of Sodium Chloride

NaCl (Normality)	Interfacial Tension (Dynes)	NaCl (Normality)	Interfacial Tension (Dynes)
0.0	1.90	0.4	0.56
0.2	0.82	0.5	0.83
0.3	0.43		

the solid soap were present, emulsions could not be obtained when equal volumes of the two phases of the last three systems were shaken together. Introduction of some of this precipitated soap favored the formation of rather unstable water-in-oil emulsions. The first two systems gave oil-in-water emulsions. The value 1.90 dynes for the interfacial tension of the equilibrium system containing no sodium chloride falls exactly on the curve of the data obtained by Harkins and Zollman[1] for 1 percent (0.033 normal) sodium oleate against benzene.

Table XIX records the interfacial tensions of benzene against 0.5 percent potassium stearate solutions containing various concentrations of potassium chloride. The presence of crystalline potassium stearate in the aqueous phases may have vitiated the values obtained but this solid soap was present when emulsification was produced with these systems; consequently the values have been reported here. The determination were carried out as with sodium oleate. See also Fig. 3.

TABLE XIX

Interfacial Tension of Benzene-Potassium Stearate Equilibrium Systems containing Various Amounts of Potassium Chloride

KCl (Normality)	Interfacial Tension (Dynes)	KCl (Normality)	Interfacial Tension (Dynes)
0.0	2.76	0.6	x
0.2	x	0.8	2.78
0.4	x	1.0	4.38

x—spontaneous emulsification prevented measurements.

[1] Harkins and Zollman: J. Am. Chem. Soc., **48**, 69 (1926).

Below potassium chloride concentration 0.8 normal the interfacial tensions were too small to be measured and oil-in-water emulsions were easily formed; solutions containing potassium chloride in concentrations ranging from 0.8 to 2.0 normal gave unstable water-in-oil emulsions, those of the higher concentrations being the most stable.

Bhatnagar[1] found that emulsions of 10 cc. paraffin oil in 10 cc. of sodium oleate solutions containing 0.080, 0.150, and 0.210 millimols of the soap could be inverted by the presence of 0.0398, 0.080 and 0.112 millimols, respectively, of barium nitrate. These systems were duplicated, using benzene, together with systems containing the same amounts of sodium oleate but in which

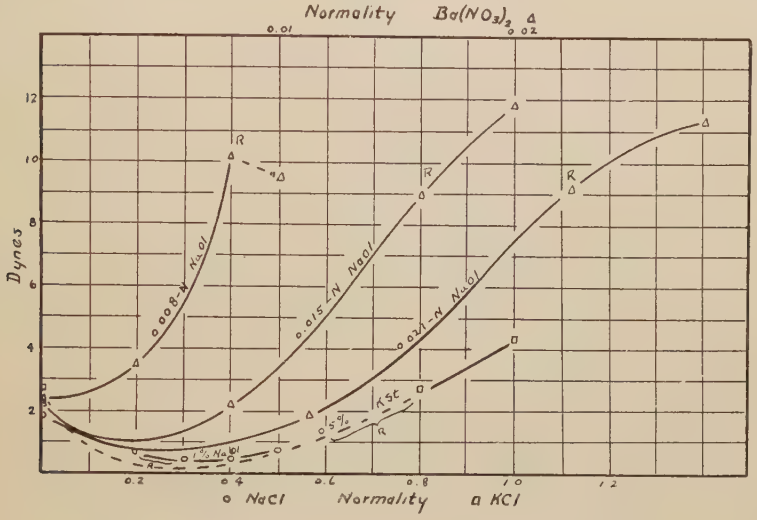

Fig. 3

there was only one-half the amount of barium nitrate necessary for the inversion of the respective emulsions, as reported by Bhatnagar. Similar systems containing 1-1/4 the inversion concentrations (R) of barium nitrate, were also prepared. Table XX records the interfacial tensions in dynes of these various systems, when determined in similar manner to those of Table XV. See also Fig. 3.

Table XX

Interfacial Tensions of Benzene-Sodium Oleate Equilibrium Systems containing Various Amounts of Barium Nitrate

NaOl Millimols	$Ba(NO_3)_2$ 0.0	1/2 R	R	1-1/4R
0.080	2.4x	3.58	10.26	9.56
0.150	2.2x	2.27	8.95	11.81
0.210	2.1x	1.90	9.17	11.34

x—values taken from data of Harkins and Zollman: J. Am. Chem. Soc., **48**, 69 (1926).

[1] Bhatnagar: J. Chem. Soc., **119**, 61 (1921).

Confirmatory emulsification tests produced oil-in-water emulsions for each 1/2 R barium nitrate concentration, and unstable inverted systems at R and 1-1/4 R concentrations. Much more stable water-in-oil emulsions were obtained when solid sodium nitrate was added to emulsions containing 1/2 R barium nitrate than when inversion was accomplished by barium nitrate alone.

Although the scope of the interfacial tension values reported here is not sufficiently great to allow extended interpretation, the data indicate that something besides low interfacial tension is necessary for the production of stable emulsions. From the emulsification tests in connection with the systems reported in Table XVIII the opinion is hazarded that one further requirement is the presence of a third phase which is capable of preventing coalescence of the dispersed droplets. Various statements occurring in the literature, which will be reviewed shortly, make it appear that colloidal soap adsorbed into the interfaces of emulsion systems is responsible for the stabilization of the oil-in-water type of emulsion. The presence of colloidal or solid material, insoluble in either phase, but which may be adsorbed into the interfaces of systems which yield water-in-oil emulsions, strongly suggests that emulsions of the latter type, produced by salting-out of the water-soluble emulsifier or by the reaction of bi- and trivalent metal salts, are stabilized for brief periods by films or skins of this finely divided solid material. The suggested reason for the comparative instability of these water-in-oil systems has already been discussed.

Discussion

The effects of electrolytes on oil-in-water emulsions stabilized by soaps should be interpreted in the light of the effects of electrolytes on solutions of soaps alone. The presence of the dispersed oil droplets may modify the behavior of the soap solution to a certain extent. The writers believe, however, that a short survey of the behavior of soap solutions in the presence of electrolytes may prove helpful in arriving at an understanding of their behavior in emulsions.

Soaps which are comparatively insoluble in water are produced when salts of the polyvalent metals are added to solutions of alkali soaps. Bhatnagar[1] maintains that the relationship between salt and soap in such instances is not stoichiometric; that adsorption compounds containing an excess of polyvalent metal ions over sodium or potassium ions in a monovalent soap, are formed. Any divergence from stoichiometric relations is, however, more likely to be due to occlusion by the curdy soap precipitate. In Bhatnagar's own work[2], in that of Parsons and Wilson[3], and in data presented here, salt and soap appear in equivalent proportions at the inversion point of emulsions. The precipitation of the insoluble soap removes the emulsifying film of the oil-in-water emulsion, which is consequently broken. Shaking then produces

[1] Private communication.

[2] Bhatnagar: J. Chem. Soc., **119**, 61 (1921).

[3] Parsons and Wilson: J. Ind. Eng. Chem., **13**, 1116 (1921).

the opposite type of emulsion, probably through the functioning of the precipitated soap as a solid emulsifier, more wetted by oil than by water. The complete solubility in the oil phase has been shown to be doubtful.

The numerous and extensive studies by McBain[1] and his co-workers have demonstrated the exceeding complexity of alkali soap solutions and have advanced several lines of evidence to prove the existence of colloidal material in all solutions except the very dilute. This colloid may be present as ionic or neutral micelles. Salmon[2] has shown that the addition of salts in small amounts reduces the proportion of ionic micelles and increases that of the neutral colloid. McBain[3] states that the effect of the addition of electrolytes with a common alkali is first to increase the formation of micelles if many simple ions are still present; second, to drive back dissociation and change the composition of the micelles and third, to diminish the hydration of the micelles. King[4] has studied the increased viscosities of soap solutions when electrolytes are added and Fischer and Hooker[5] have obtained interesting results on the viscosity increase as a preliminary step to the salting-out of soaps by various electrolytes. McBain, Willavoys and Heighington[6] have made a thorough investigation of the viscosity increase in the case of sodium palmitate. The enormous increase in viscosity is explained to be the result of partial dehydration (a concentrating effect) of the micelles and the increased amount of colloidal material. Fischer and Hooker state that the initial increase in viscosity occurs at the same potassium ion concentrations, when potassium oleate is salted out by potassium salts of different anion valencies, while McBain and Pitter[7] conclude that in the completed salting-out of soaps "the salts do not replace each other equivalent for equivalent, but rather mol for mol, irrespective of their valency." It is the universal observation that a great decrease in the viscosity of the soap attends the addition of the last of the salt required to salt-out the soap.

Bhatnagar[8] is to be credited with perhaps the most accurate published work on the inversion of emulsions by electrolytes. In the last paper just referred to he says that "it is difficult to draw hard and fast lines between the effects of univalent electrolytes and bi- and ter-valent electrolytes on soap solutions, as both of these are adsorption phenomena. On the solubility hypothesis sodium chloride ought to be capable of changing the type of emulsion as well as barium chloride. This is, however, contrary to all experience and the multivalent ions alone are known to cause reversal of type." If these effects were really simple adsorption phenomena, then it *should be possible*

[1] McBain: "The Study of Soap Solutions," Chap. XVI, Bogue's "Colloidal Behavior,' 410 (1924).
[2] Salmon: J. Chem. Soc., **121**, 711 (1922).
[3] McBain: Rep. Brit. Ass. Adv. Sci., **1920**, 1-154A.
[4] King: J. Soc. Chem. Ind., **41**, 147T (1922).
[5] Fischer and Hooker: "Soaps and Proteins," 116 (1921).
[6] McBain, Willavoys and Heighington: J. Chem. Soc., **1927**, 2689.
[7] McBain and Pitter: J. Chem. Soc., **1926**, 893.
[8] Bhatnagar: J. Chem. Soc., **117**, 542 (1920); **119**, 61, 1766 (1921).

"to draw hard and fast lines" between uni- and polyvalent ions. Furthermore, Tartar, Duncan, Shea and Ferrier[1], and Lothrop and Pettengill[2] in this laboratory have made some quantitative studies on the inversion of emulsions by salts of the same metal as the soap. Mead and McCoy[3] reported such an observation but evidently did not carry through complete experimental tests on the phenomenon.

From the abundance of evidence presented on the increase of the colloidal nature of soap solutions together with that which indicates the stabilizing influence of small amounts of sodium chloride on sodium soap emulsions[4] it seems that soap owes its emulsifying power primarily to its colloidal nature and that by increasing these colloidal properties, sodium chloride in small amounts thus promotes oil-in-water emulsion stabilization. Harkins and Zollman[5] have shown that sodium chloride reduces remarkably the benzene-aqueous sodium oleate interfacial tension. This is due to the increased adsorption of the surface-active sodium oleate in the presence of the chloride, as was shown to take place through the work of Dubrisay[6]. Thermodynamically, the lower interfacial tension makes the extension of the interface by the formation of droplets easier, but the stabilization of these droplets has been shown to depend upon still other factors.

Sodium chloride probably does not have the antagonistic effect for calcium chloride attributed to it by Clowes; it does lower the interfacial tensions of soap solutions against oil phases, but this in no wise interferes with the precipitation of the soap on the addition of salts of polyvalent metals. Either alkali salts or salts of polyvalent metals, when present in soap solutions in sufficient quantities, produce soaps which are insoluble in water and stabilize water-in-oil emulsions if they are sufficiently wetted by the oil phase.

Because the physico-chemical reasons for the inversion of emulsions by electrolytes are still in doubt, the complete explanation of emulsification when soaps are used for stabilizers, is at present lacking. Few aspects of the emulsion problem are so intriguing as inversion because of its fundamental relationship to emulsion theory. However, as has been pointed out before, the tendency to generalize has been a pitfall in the theoretical treatment of emulsions. There are too many possible variables in a system so complex as an emulsion to lay too much general emphasis upon the results of any one study.

Summary

1. The distribution of soap emulsifiers between the immiscible phases of emulsions is a type-determining factor of such systems; it applies to soaps of both univalent and polyvalent metals.

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[1] Tartar, Duncan, Shea and Ferrier: J. Phys. Chem., 33, 435 (1929).

[2] Tartar, Lothrop and Pettengill: J. Phys. Chem., 34, 000 (1930).

[3] Mead and McCoy: "Colloid Symposium Monograph," 4, 44 (1926).

[4] Clayton: "Margarine," 72, (1920); Ayres: Chem. Met. Eng., 22, 1061 (1920); Herschel: U. S. Bur. Standards Tech. Papers, No. 66, 17 (1917).

[5] Harkins and Zollman: J. Am. Chem. Soc., 48, 69 (1926).

[6] Dubrisay: Compt. rend., 182, 1217 (1926).

2. Distribution of soap is controlled by factors influencing solubility and wettability, such as temperature, phase-volume relationships, mechanical treatment, the presence of electrolytes, etc.

3. Oil-in-water emulsions are stabilized by soaps that are chiefly present in the aqueous phase; the soaps are probably colloidal at the interfaces of such emulsions. Soaps that are more easily wetted by the "oil", or are chiefly in solid or colloidal condition in the non-aqueous phase, temporarily stabilize water-in-oil emulsions. These conditions apply to soaps of both univalent and polyvalent metals. The concentration of soap at emulsion interfaces may be regarded as constituting a third phase of the system.

4. Low interfacial tensions aid the dispersion of droplets of one liquid in another, but must be accompanied by material capable of forming permanent films around the droplets, in order that the emulsion be stable.

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